

Excess Thermodynamic Parameters of Binary Liquid Mixtures at 303K

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(Received on: January 18, 2013)

ABSTRACT

The experimental density (ρ), viscosity (η) and velocity (U) have been measured for binary liquid mixtures of Methylmethacrylate with methanol, cyclohexane and 1,4-dioxane at the temperature 303K. These data were used to determine the excess adiabatic compressibility(β_a^E), excess free length(L_f^E), excess free volume(V_f^E), excess internal pressure(π_i^E), excess relaxation time(τ^E), excess acoustic impedance(Z_a^E) and excess Gibbs'(ΔG^E). From these excess parameters, the nature and the strength of molecular interactions in these binary systems are discussed.

Keywords: Ultrasonic velocity, acoustical parameters, molecular interactions, Methylmethacrylate, methanol, cyclohexane, 1,4-dioxane, binary mixtures and excess parameters.

1. INTRODUCTION

Ultrasonic study is very much useful for characterizing the Physico-chemical behavior of liquids mixtures and measurements are used to study molecular interactions in the Liquids^{1, 2}. The method of studying molecular interaction from the knowledge of variation of acoustic parameters along with their excess values with change in mole fraction gives an insight into the molecular process^{3, 4}. The increase or decreases in ultrasonic velocities have

been employed in understanding the nature of molecular interaction in the pure liquids, binary mixtures and ternary mixtures⁵. The study of liquid mixtures containing of polar and non-polar components find applications in industrial and technological process⁶. The number of studies on the thermodynamics properties of binary and ternary mixtures has increased in recent years due to industrial applications⁷⁻¹³. The mixing of different components gives rise to solutions that generally do not behave ideally¹⁴. The deviation from ideally is expressed by many

thermodynamic variables, particularly by excess properties¹⁵. Further these properties have been widely used to study the molecular interaction between the various species in the mixture^{16,17}.

In present study ultrasonic velocity, density and viscosity were measured experimentally for the binary systems namely *Methylmethacrylate +methanol*, *Methylmethacrylate +1,4-dioxane* and *Methylmethacrylate +cyclohexane* mixtures at 303K. From the measured data, related acoustical and thermodynamic excess parameters such as, the excess adiabatic compressibility(β_a^E), excess free length(L_f^E), excess free volume(V_f^E), excess internal pressure(π_i^E), excess relaxation time(τ^E), excess acoustic impedance(Z_a^E) and excess Gibb's(ΔG^E) have been computed and the results of excess parameters are analyzed in the light of molecular interactions in the binary mixtures.

2. EXPERIMENTAL DETAILS

The liquids Methylmethacrylate (solute) and methanol, 1,4-dioxane and cyclohexane (solvents) were of Analar grade and redistilled before use. The binary mixture of different mole fraction of the two components in the Systems-I:- Methylmethacrylate +methanol, Systems-II:- Methylmethacrylate +1,4-dioxane and Systems-III:- Methylmethacrylate +cyclohexane were prepared immediately before use. The velocity of ultrasonic wave (U) of frequency 10MHz and density (ρ) in these mixtures were measured by employing Ultrasonic Time Interferometer, UTI-10 (Innovative instruments, Hyderabad), and hydrostatic sinker method in the temperature range 10-40°C. Ultra thermostat

U-10 maintained temperature of samples, constant to 0.1°C. A specially designed and fabricated double walled, metallic ultrasonic cell and glass cell along with 6- digit monopan balance permitted to achieve accuracy of 1 in 10⁴ m/s in velocity and 1 in 10⁴ gm in density measurement. An Ostwald's viscometer was used for the viscosity (η) measurement of pure liquids and liquid mixtures with an accuracy of 0.0001Nm⁻²s. The viscometer was calibrated before used. All the precautions were taken to minimize the possible experimental error.

The various acoustical parameters such as Adiabatic compressibility (β_a), Intermolecular free length (L_f), Free volume (V_f), Internal pressure(π_i), Relaxation time(τ) and Gibb's energy(ΔG) has been calculated from the ultrasonic velocity (U), the density (ρ) and viscosity(η) of the medium using the following standard equations as:

$$\beta_a = 1 / (U^2 \rho) \quad (1)$$

$$L_f = K_T (\beta_a)^{1/2} \quad (2)$$

$$V_f = [M_{\text{eff}} U / K \eta]^{3/2} \quad (3)$$

$$\pi_i = bRT (K \eta / U)^{1/2} (\rho^{2/3} / M^{7/6}) \quad (4)$$

$$\Delta G = (K_B T) \log (K_B T \tau / h) \quad (5)$$

$$Z = U \rho \quad (6)$$

$$\tau = (4/3) \beta_a \eta \quad (7)$$

Where K_T – is a Jacobson's constant. Where M_{eff} is the effective molecular weight ($M_{\text{eff}} = \sum m_i x_i$, in which m_i and x_i are the molecular weights and the mole fraction of the individual constituents respectively). K

is a temperature independent constant which is equal to 4.28×10^9 for all liquids, b stands for cubic packing which is assumed to be 2 for all liquids, and T is the absolute temperature. K_B is the Boltzmann's constant and h has usual meaning.

Excess parameters (A^E) represent the difference between the parameters of real

mixtures ($A_{exp.}$) and those corresponding to an ideal mixture ($A_{id.}$).

$$A^E = A_{exp.} - A_{id.} \quad (8)$$

Where $A_{id.} = \sum A_i X_i$, $i = 1, 2, 3, n$.
 A_i is any acoustical parameters and x_i the mole fraction of the liquid components.

Table – 1: Comparison of experimental values of density (ρ), viscosity (η) and Ultrasonic Velocity (U) of pure liquids at 303K with literature values

Sr No.	Pure Liquids	Density (ρ) (Kg m ⁻³)		Viscosity (η) (10 ⁻³ NSm ⁻²)		Velocity (U) (m/s)	
		Expt.	Literature	Expt.	Literature	Expt.	Literature
1.	<i>Methylmethacrylate</i>	947.40	-----	0.4797	-----	1141.00	-----
2.	<i>Methanol</i>	776.10	777.70	0.5150	0.5020	1086.00	1087.00
3.	<i>1,4 Dioxane</i>	1027.40	1028.10	0.8154	1.0100	1324.00	1323.00
4.	<i>Cyclohexane</i>	772.30	763.70	0.6887	0.6895	1240.00	1243.30

Table -2: The computed excess thermodynamic parameters for β_a^E , L_r^E & V_r^E at 303K for the Systems-I, II & III, respectively

MOLE FRACTION		$\beta_a^E * 10^{-10}$ (Pa ⁻¹)			$L_r^E * 10^{-10}$ (m)			$V_r^E * 10^{-8}$ (m ³ mol ⁻¹)		
X1	X2	METHA-NOL	DIOX-ANE	CYCLO-HEXANE	METHA-NOL	DIOX-ANE	CYCLO-HEXANE	METHA-NOL	DIOX-ANE	CYCLO-HEXANE
0	1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.9	-0.1062	-0.1062	-0.1000	-0.5935	0.0505	0.0004	-0.1854	-0.2482	-0.1979
0.2	0.8	-0.1423	-0.1423	-0.0411	-0.0034	0.0534	0.0185	-0.3715	-0.4768	-0.3998
0.3	0.7	-0.1485	-0.1485	-0.0002	-0.0033	0.0505	0.0000	-0.5677	-0.6927	-0.6041
0.4	0.6	-0.1187	-0.1187	-0.0675	-0.0022	0.0450	0.0023	-0.7397	-0.8879	-0.8051
0.5	0.5	-0.2193	-0.2193	-0.1319	-0.0055	0.0353	0.0046	-0.9341	-1.0590	-1.0111
0.6	0.4	-0.0924	-0.0924	-0.0802	-0.0014	0.0342	0.0028	-1.1341	-1.2819	-1.2059
0.7	0.3	-0.0888	-0.0888	-0.1295	-0.0015	0.0290	0.0045	-1.3517	-1.4762	-1.4254
0.8	0.2	-0.0089	-0.0089	0.2249	0.0008	0.0260	0.0077	-1.5465	-1.6805	-1.6153
0.9	0.1	0.0730	0.0730	0.1198	0.0031	0.0175	0.0041	-1.5953	-1.8828	-1.8218
1	0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table -3: The computed excess thermodynamic parameters for π_i^E , Z_a^E & ΔG^E at 303K for the systems-I, II & III, respectively

MOLE FRACTION		$\pi_i^E \times 10^6$ (Pa.S)			$Z_a^E \times 10^6$ (Kgm ⁻² s ⁻²)			$\Delta G^E \times 10^{-20}$ (KJmole ⁻¹)		
X1	X2	METHA-NOL	DIOX-ANE	CYCLO-HEXANE	METHA-NOL	DIOX-ANE	CYCLO-HEXANE	METHA-NOL	DIOX-ANE	CYCLO-HEXANE
0	1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.9	-113.3085	7.1137	6.1362	-0.0015	-0.0324	-0.0021	0.0079	0.0117	0.0079
0.2	0.8	-63.9790	15.4239	12.7981	-0.0017	-0.0505	-0.0057	0.0160	0.0260	0.0167
0.3	0.7	-176.490	23.4651	20.2001	-0.0015	-0.0566	0.0011	0.0248	0.0360	0.0237
0.4	0.6	222.0391	29.3213	31.2450	-0.0095	-0.0568	0.0075	0.0324	0.0437	0.0306
0.5	0.5	-156.0513	33.6925	33.4489	-0.0101	-0.0319	-0.0160	0.0387	0.0486	0.0432
0.6	0.4	-123.5547	42.8727	40.9208	-0.0117	-0.0530	-0.0123	0.0489	0.0591	0.0502
0.7	0.3	-78.6502	49.3549	71.0017	-0.0069	-0.0510	-0.1280	0.0563	0.0668	0.0593
0.8	0.2	-36.9876	56.6461	55.5067	-0.0145	-0.0525	-0.0250	0.0650	0.0757	0.0695
0.9	0.1	-9.6031	66.0243	62.3106	-0.0179	-0.0365	-0.0209	0.0734	0.0816	0.0753
1	0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table -4: The computed excess thermodynamic parameters for τ^E at 303K for the systems-I, II & III, respectively

MOLE FRACTION		$\tau^E \times 10^{-12}$ (S)		
X1	X2	METHANOL	DIOXANE	CYCLOHEXANE
0	1	0.0000	0.0000	0.0000
0.1	0.9	0.0303	0.0433	0.0301
0.2	0.8	0.0591	0.0937	0.0623
0.3	0.7	0.0912	0.1290	0.0878
0.4	0.6	0.1180	0.1569	0.1108
0.5	0.5	0.1390	0.1735	0.1593
0.6	0.4	0.1774	0.2139	0.1834
0.7	0.3	0.2037	0.2428	0.2174
0.8	0.2	0.2354	0.2780	0.2561
0.9	0.1	0.2660	0.3002	0.2748
1	0	0.0000	0.0000	0.0000

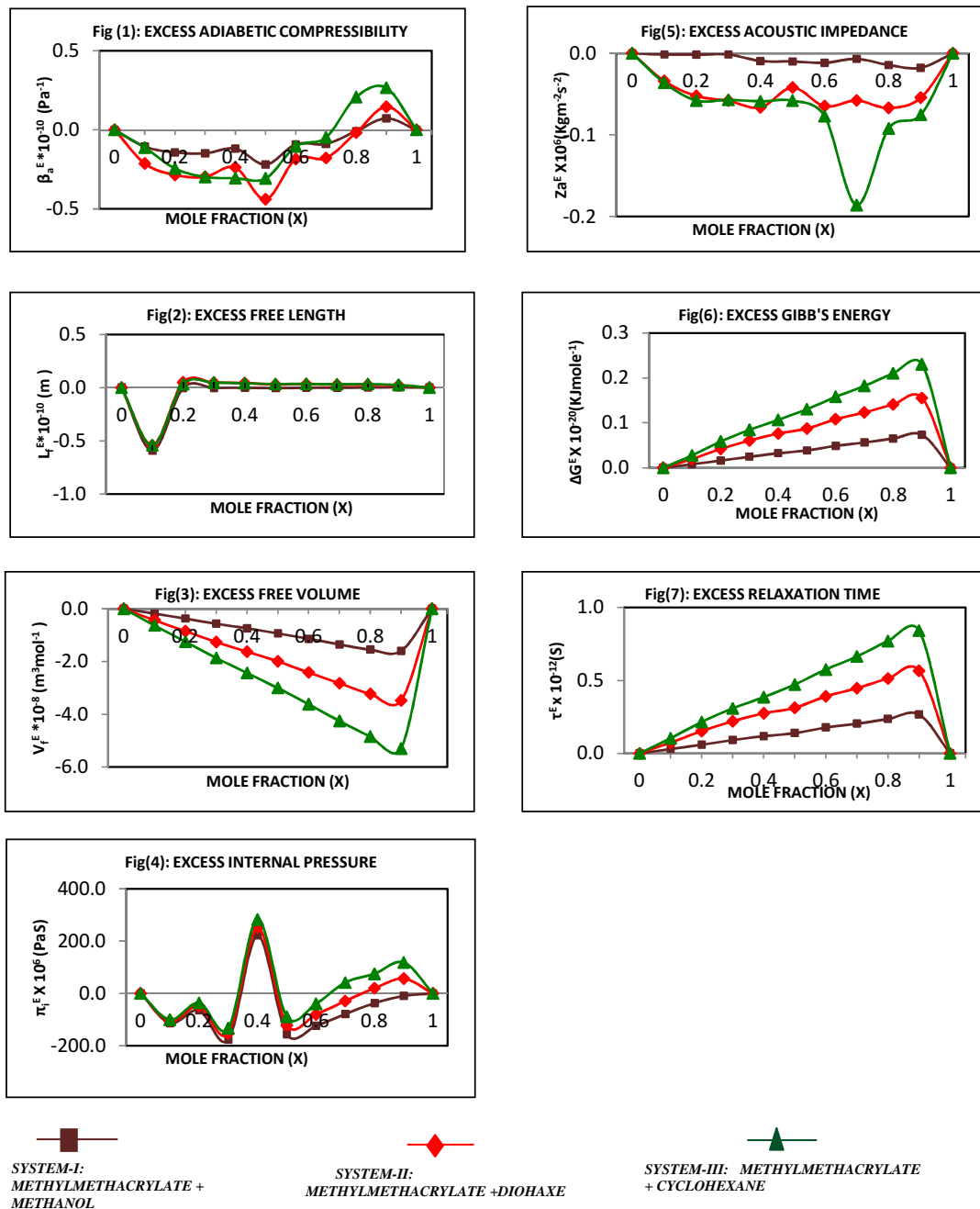


Fig.1-7: Graphs for excess parameters of adiabatic compressibility (β_a^E), free length (L_r^E), free Volume (V_r^E), Internal pressure (π_i^E), relaxation time (τ_r^E), acoustic impedance (Z_a^E) and Gibb's Energy (ΔG^E) for the systems-I, II & III, respectively at 303K.

3. RESULT AND DISCUSSION

The values of ultrasonic velocity (U), density (ρ) and viscosity (η) for the pure liquids used in this paper are compared with literature values and shown in the Table-1. Table: 2-4 shows, the variation of excess compressibility (β_a^E), excess free length (L_f^E), excess internal pressure (π_i^E), excess acoustic impedance (Z^E), excess free volume (V_f^E) and excess Gibbs free energy (ΔG^E) for different mole concentration of solute : methylmethacrylate and solvents : methanol, cyclohexane and 1,4-dioxane respectively, for the system-I: (methylmethacrylate+ methanol), system -II: (methylmethacrylate +1,4-dioxane) and system-III: (methylmethacrylate+ cyclohexane) respectively.

The excess adiabatic compressibility (β_a^E) is overall negative over the entire composition range of the mixture for all the systems, except at the composition 0.9 of the mixture. The negative value of excess adiabatic compressibility indicate that the liquid mixture is less compressible than the pure liquids forming the solution and the molecules in this mixture are more tightly bound in the liquid mixture than in pure liquids. Thus negative value of excess adiabatic compressibility of this system indicates strong specific interaction between the component molecules and interstitial accommodation of small molecules in the voids created by bigger molecules.

The excess free volume (V_f^E) is negative for all the systems over the entire composition range of the mixture. The negative value of excess free volume (V_f^E) for all the systems suggests the component molecules are more closed together in the

liquid mixture than in the pure liquids forming the mixture, indicating that, strong attractive interactions between component molecules such as hydrogen bonding and dipole-dipole interactions.

The variation of excess free length (L_f^E) is overall negative over the entire range of composition, for the system-I: (methylmethacrylate+methanol) and positive, for the system -II : (methylmethacrylate+1,4-dioxane) & system-III:(methylmethacrylate+ cyclohexane). The negative value of excess free length (L_f^E) for the system-I: (methylmethacrylate+methanol), indicates structural readjustment in the liquid mixture toward a less compressible phase of fluid and closer packing of the molecule^{18, 19}. This aspect further supports the variation of other excess parameters, excess internal pressure (π_i^E), excess acoustic impedance (Z^E) and excess Gibbs free energy (ΔG^E).

4. CONCLUSION

In this paper, density, ultrasonic velocity and viscosity data are reported for the binary mixture of methylmethacrylate+ methanol, methylmethacrylate+1, 4-dioxane and methylmethacrylate cyclohexane at the temperature 303K. The excess thermodynamic parameter such as excess compressibility (β_a^E), excess free length (L_f^E), excess internal pressure (π_i^E), excess acoustic impedance (Z^E), excess free Volume (V_f^E) and excess Gibbs free energy (ΔG^E) for different mole concentration of solute for the above binary mixtures are evaluated and these parameters suggests the presence of weak molecular interactions.

This molecular interaction is primarily of dipole –induced dipole type, which becomes stronger in the system- I:(methylmethacrylate+methanol) and weaker in the system- II : (methylmethacrylate+1, 4-dioxane) and III : (methylmethacrylate cyclohexane). Further in all the systems, the non-polar cyclohexane and 1, 4-dioxane behaves as structure breaker for associated methylmethacrylate.

5. ACKNOWLEDGEMENT

The author, VDB ([File No.: F-47-919/09(WRO)]) is very much thankful to the university Grant commission for providing financial assistance in the form of minor research project (MRP).

REFERENCES

1. Kannappam V *et al.*, *Indian J Pure & Applied Physics*, 44, pp:670-676 (2006).
2. Voleisiene B & Voleisis A, *Ultragarsas*, 63(4), pp: 7-9 (2008).
3. Jain D V S & Dhar N S, *Ind J Tech*, 310, pp: 620 (1992).
4. Amalandu Pal & Gurcharan Das, *J. Pure & Applied Ultrasonics*, 21, pp: 9 (1990).
5. Mistry A A, Bhandakkar V D & Chimankar O P, *Jour. of Chem. & Pharma. Res*, 4(1), pp: 170-174 (2012).
6. Tabhane V A & Patki B A, *Indian J. Pure & Applied Physics*, 23, pp:58 (1985).
7. Venkatesu P & Ramadevi R S, *J. Pure & Applied Ultrasonics*, 18, pp: 16 (1996).
8. Bhandakkar V D *et al.*, *Journal of Chemical and Pharmaceutical Research*, 2(4) 873-877 (2010).
9. Bhandakkar V. D., *Adv. Applied Sci. Res.* 2(3), pp-198-207 (2011).
10. Bedare G R, Bhandakkar V D & Suryavanshi B M, *International J of Appl Phy and Math.*, 2(3), pp: 197-200 (2012).
11. Bedare G R, Bhandakkar V D & Suryavanshi B M, *Journal of Chemical and Pharmaceutical Research*, 4(2), pp: 1028-1032 (2012).
12. Bedare G R, Bhandakkar V D & Suryavanshi B M, *European J of Appl Eng & Scientific Res, Scholar Research Library*, 1(1), pp: 1-4 (2012).
13. Bhandakkar V D, *International organization of scientific research, J of Appl Phy*, 1(5), pp: 38-43 (2012).
14. John George, Nandhibatla V. Sastry, Sunil R. Patel, Mahendra K Valand, *J Chem Eng*, 47, pp: 262 (2002).
15. Sravan Kumar D & Krishna Rao D, *Indian J Pure & Applied Physics*, 45, pp: 210-220 (2007).
16. Ali A & Soghra, *Indian J physics*, 76B (1), pp: 23 (2002).
17. Ali A, Abida, Hyder S & Nain A K, *Indian J Pure & Applied Physics*, 76B, pp: 661 (2002).
18. Oswal S L & Patel N B, *J Chem Data*, 45, pp: 225 (2000).
19. Rama Rao G V, Sarma Viswanatha A, & Rambabu C, *Indian J Pure & Applied Physics*, 42, pp: 820 (2004).